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Title: Neptunium-236 Production- Irradiated Highly Enriched Uranium Target

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SUBJECT: NEPTUNIUM-236 PRODUCTION – IRRADIATED HIGHLY ENRICHED URANIUM TARGET

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Background

In August 2018 two ~200 mg 93% ^{235}U foils, UO-1 and UO-2, were irradiated at Lawrence Berkeley National Laboratory with the aim of producing ^{236}Np (1.53×10^5 y half-life). The meta-stable isotope, ^{236m}Np (22.5 h half-life), could be observed immediately post-irradiation by gamma spectroscopy (642 keV). In December 2018, the samples were shipped to LANL for additional destructive analysis, which included ^{236}Np and ^{237}Np measurements. In April 2019, a piece of an un-irradiated disc (73 mg) of similar target material was sent to LANL from LBNL. This report summarizes the dissolution of the targets and subsequent actinide analyses performed in 2019.

Sample Unpacking and Initial Mass Measurements

Due to partial sample oxidation unpacking the uranium discs from the Mylar covered aluminum foils became a two person operation, and A.J. Gaunt (C-IIAC) assisted I. May with this procedure. Orange/brown Mylar appeared to be glued to the outer aluminum foil which was wrapped around the individually wrapped uranium discs. The UO-2 sample still contained the nickel monitor foil which was set aside. The extent of uranium metal oxidation increased along the series UO-2<UO-1<un-irradiated foil. The un-irradiated foil was too heavily oxidized, as evidence by the large amount of dark power, for a confirmatory mass measurement. The recorded mass values of the UO-1 and UO-2 metal discs were 219.7 and 200.1 mg, respectively, with STDEV of three replicate measurements <0.05 %.

Sample Dissolution

Optima acids and >18 MOhm-cm water were utilized for sample dissolutions. Care was taken to transfer both the metal discs and as much oxide as possible into 400 mL Teflon beakers for dissolution. 4 M HNO_3 was used to wash across the oxide from within the aluminum foil, although some oxide was visibly bound to the adhesive used to stick the Mylar to the aluminum foil. As previously stated, oxidation was most pronounced across the series UO-2<UO-1<un-irradiated foil. A mixture of 4 M HNO_3, conc. HNO_3, a minimum HCl and heat were used to dissolve the samples. HCl dissolved up the metal and the solutions were initially green in color due to the presence of U(IV). The nitric acid served to both control the HCl-metal reactivity and dissolve up the oxide material. Addition of excess 4 M HNO_3 and heat allowed the residual HCl to be driven off, oxidize the U(IV) to U(VI), and served as the acid for final solution preparation. All 3 yellow solutions were prepared in Teflon bottles, with sample masses given in the table below. The STDEV of three replicate measurements was <0.01 %.

Table 1. Solution masses for three highly enriched uranium foils dissolved in 2019.

Sample	Solution Mass (g)
Un-irradiated foil	55.762
UO-1	109.486
UO-2	111.178

Sample Analysis and Results

To get an initial estimate of the plutonium and neptunium concentration and isotopic composition, an untraced aliquot of each sample was purified using a combination of solvent extraction and anion exchange chromatography. An initial lanthanum fluoride co-precipitation was used to concentrate the Pu and Np. After a reduction step with Fe(II) chloride and hydroxylamine, Np^{IV} was extracted using a 0.5 M solution of TTA (TTA = 2-thenoyltrifluoroacetone) in xylenes. The Np was back-extracted into 8 M HNO_3 and the aqueous solution evaporated. A subsequent anion exchange column in a chloride system was used to provide additional separation from uranium. Plutonium was recovered from the aqueous phase of the solvent extraction by lanthanum fluoride precipitation and then further purified by a series of two anion exchange columns.

Based on the results of the untraced analysis, aliquots of the target solutions were traced with ^{242}Pu (NIST 4334G) and ^{237}Np (NIST 4341) and purified in order to determine the concentrations of plutonium and neptunium in the target; the un-irradiated foil was traced with ^{236}Np (in-house, well-calibrated tracer). After purification, the traced plutonium fractions were electroplated and measured by alpha spectrometry using an Ortec alpha spectrometer equipped with a 300 mm^2 Si-detector (Figures 1 and 2, Table 2). UO-1 contained 1.93 x 10^8 (± 0.7%) atoms of ^{236}Pu and 2.42 x 10^8 (± 1.9%) atoms of ^{238}Pu. UO-2 contained 7.79 x 10^8 (± 0.6%) atoms of ^{236}Pu and 1.59 x 10^9 (± 1.2%) atoms of ^{238}Pu, consistent with a longer irradiation time. The ^{236}Pu/^{238}Pu atom ratios were distinctly different between the two targets, with 0.80(2) measured for UO-1 and 0.49(1) measured for UO-2. The un-irradiated foil was also measured, with ^{236}Pu and ^{238}Pu both being below detection limits. The $^{239+240}$Pu activity in the three samples is shown in Table 2 and reflects increasing irradiation time with higher activity in the longer irradiated samples. Note that the un-irradiated target does include $^{239+240}$Pu activity well above the detection limit.

The untraced neptunium fractions were analyzed by ICP-MS and the neptunium isotopic composition was characterized (Table 3). The measured ^{236}Np/^{237}Np atom ratio is 0.21(1) for UO-1 and 0.65(3) for UO-2. Total atoms per target were calculated for ^{236}Np and ^{237}Np (Table 3); ^{235}Np was not quantified due to the presence of trace amounts of HEU in the aliquots – even a very small amount of HEU has the potential to significantly interfere with a mass spectrometry measure of ^{235}Np due to the high amount of ^{235}U. UO-1 contained 1.28 x 10^8 (± 2.58%) atoms of ^{236}Np and 6.03 x 10^8 (± 6.7%) atoms of ^{237}Np. UO-2 contained 4.93 x 10^8 (± 1.8%) atoms of ^{236}Np and 7.57 x 10^8 (± 4.3%) atoms of ^{237}Np. The un-irradiated target contained 1.60 x 10^8 (± 3.6%) atoms of ^{237}Np and no detectable ^{236}Np.
Untraced uranium fractions of irradiated and un-irradiated targets were purified for uranium using extraction chromatography (Eichrom UTEVA) resin and analyzed by ICP-MS to determine uranium isotopic composition (Table 4). There is no measurable ^{236}U in any of the samples (Figure 3); counts measured at the 236 position are entirely caused by tailing from the neighboring high signal ^{235}U peak. The impact of this is that when the Np fractions are measured, if there is any residual U from the target, it

can be asserted that all counts in the 236 peak are from ^{236}Np and a correction for ^{236}U is not necessary. The isotopic composition of uranium was unchanged due to irradiation; the isotopic compositions of U in UO-1 and UO-2 are identical to that in the un-irradiated target.

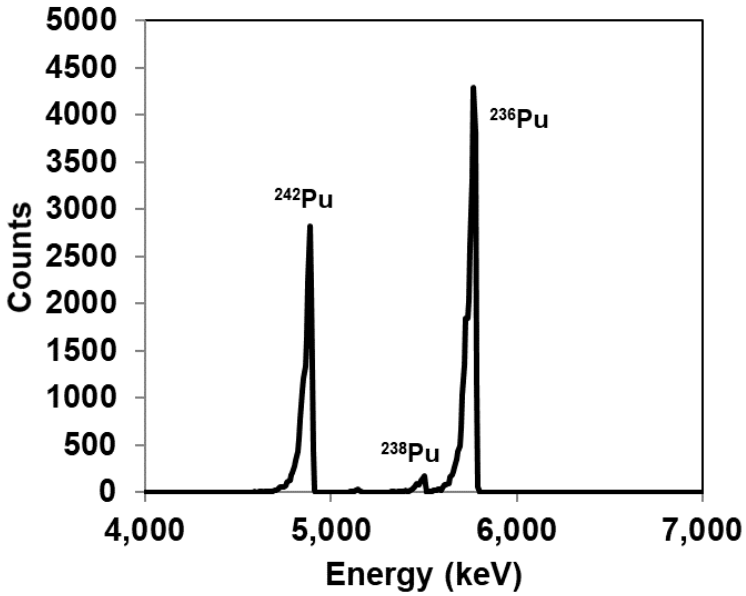

Figure 1. Alpha spectrum of traced plutonium fraction of UO-1.

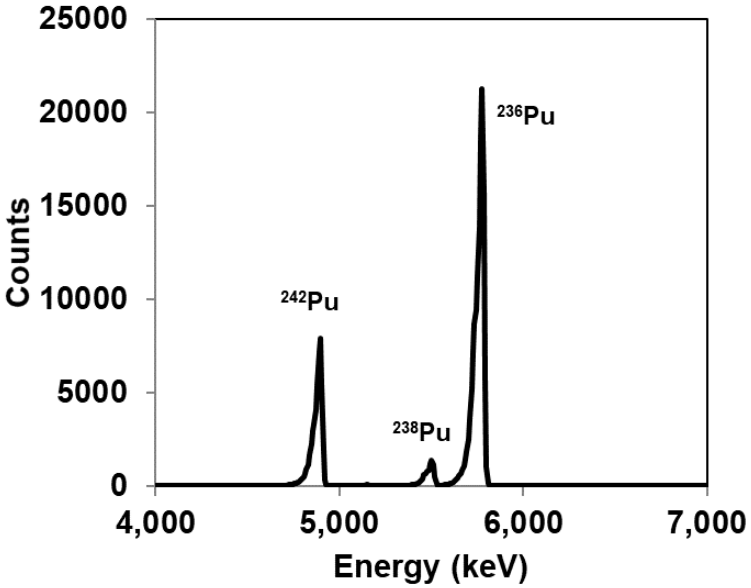

Figure 2. Alpha spectrum of traced plutonium fraction of UO-2.

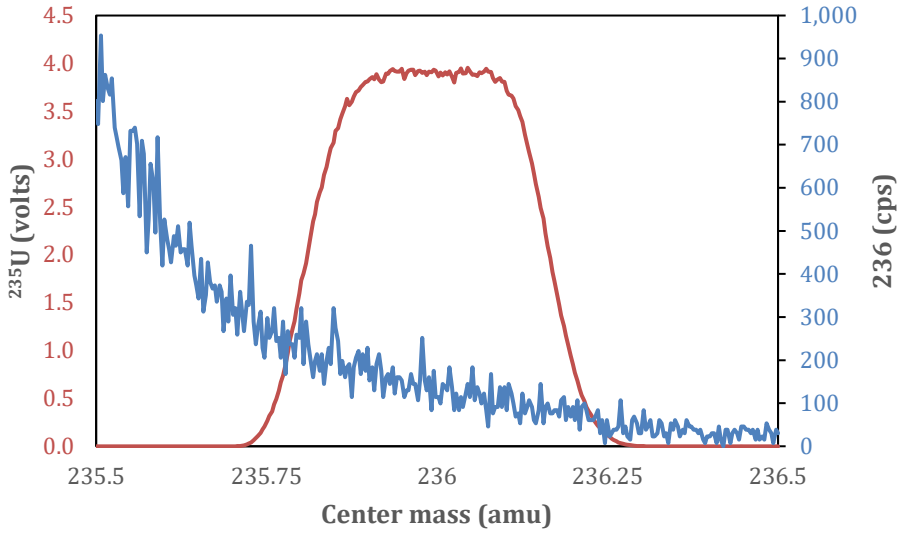

Figure 3. Peak shape and tail for uranium fraction of UO-2. All counts at 236 can be attributed to tail from ^{235}U and are not caused by measurable ^{236}U. Peak and tail shapes are similar for UO-1 and the un-irradiated target.

Table 2. Plutonium concentrations measured for the un-irradiated target, UO-1 and UO-2. Values are reported on a per target basis, with uncertainties at $k = 1$. The reference date is 7/8/19.

Sample	$^{239+240}$Pu (dpm)	^{236}Pu (atoms)	^{238}Pu (atoms)	^{236}Pu (fg)	^{238}Pu (fg)
Un-irradiated Target	0.10(1)	$L_D = 1.9 \times 10^4$	$L_D = 5.8 \times 10^5$	—	—
UO-1	0.48(2)	1.93×10^8 (± 0.7%)	2.42×10^8 (± 1.9%)	75.7(5)	96(2)
UO-2	1.15(6)	7.79×10^8 (± 0.6%)	1.59×10^9 (± 1.2%)	305(2)	630(8)

Table 3. Neptunium isotopic composition and concentrations measured for the un-irradiated target, UO-1 and UO-2. Values are reported on a per target basis; isotope ratios are reported as atom ratios, and uncertainties at $k = 1$. The reference date is 7/8/19.

Sample	^{236}Np/^{237}Np	^{236}Np (atoms)	^{237}Np (atoms)	^{236}Np (fg)	^{237}Np (fg)
Un-irradiated Target	—	$L_D = 1.9 \times 10^7$	1.60×10^8 (± 3.6%)	—	63(2)
UO-1	0.21(1)	1.28×10^8 (± 2.6%)	6.03×10^8 (± 6.7%)	50(1)	237(16)
UO-2	0.65(3)	4.93×10^8 (± 1.8%)	7.57×10^8 (± 4.3%)	193(3)	298(13)

Table 4. Uranium isotopic composition for the un-irradiated target, UO-1 and UO-2. Isotope ratios are reported as atom ratios.

Sample	**$^{234}U/^{238}U$**	**$^{235}U/^{238}U$**
Un-irradiated Target	0.2210(2)	17.614(18)
UO-1	0.2209(1)	17.605(5)
UO-2	0.2210(1)	17.615(4)

Summary and Conclusions

The $^{236}Pu/^{236}Np$ ratio in the irradiated targets is a measure of the $^{236m}Np/^{236g}Np$ production rate during the irradiation. For the two targets UO-1 and UO-2 the $^{236}Pu/^{236}Np$ atom ratios are 1.52(4) and 1.58(3) respectively. These numbers are statistically identical, even at the 1SD level. This suggests that the production ratio of the two ^{236}Np isomers can be accurately estimated for these irradiation conditions.

The presence of significant amounts of ^{237}Np in the un-irradiated target requires calculation of the ^{237}Np created during the irradiations. Additionally, the distinctly different masses of the un-irradiated and irradiated targets requires consideration. As described in the Sample Unpacking Section, an accurate mass of the un-irradiated target could not be taken at LANL due to surface oxidation. However, using the reported mass of 73 mg and the measured masses of UO-1 and UO-2, it is possible to calculate atoms ^{237}Np/gram target for each sample, and recalculate ^{237}Np atoms per target from the irradiation (denoted $^{237}Np^*$). Taking these calculations into account, Table 3 becomes Table 5; the $^{236}Np/^{237}Np^*$ ratios are significantly different from those in Table 3 with values of 1.05(38) and 1.55(18) for UO-1 and UO-2 respectively. Note that the propagated uncertainties on $^{237}Np^*$ are significantly higher than on measured ^{237}Np because the dominant source of ^{237}Np in the samples is from the initial target and consequently the calculated $^{237}Np^*$ is relatively minor compared to the ingoing ^{237}Np from the target.

Table 5. Neptunium isotopic composition and concentrations measured for the un-irradiated target, UO-1 and UO-2 taking into account ^{237}Np present in un-irradiated target. Values are reported on a per target basis; isotope ratios are reported as atom ratios.

Sample	**$^{236}Np/^{237}Np^*$**	**^{236}Np (atoms)**	**$^{237}Np^*$ (atoms)**	**^{236}Np (fg)**	**$^{237}Np^*$ (fg)**
UO-1	1.05(38)	1.28×10^8 (± 2.6%)	1.22×10^8 (± 36%)	50(1)	48(17)
UO-2	1.55(18)	4.93×10^8 (± 1.8%)	3.19×10^8 (± 12%)	193(3)	125(14)